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Heterogeneous Catalysis

Hydrogen Dissociation by Gold Clusters**

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Hydrogenation reactions are a major contributor (almost 6%) to current chemical processes in terms of the market sales of catalysts in the world.[1] Although gold catalysts have recently shown great potential for selective oxidation,[2–5] they are still regarded as being inferior to palladium and platinum catalysts in hydrogenation.[6–9] In 1966, Wood and Wise reported on the hydrogenation of cyclohexene over a gold film electroplated on a Pd–Ag alloy thimble,[6] which was the first investigation of a hydrogenation reaction over a gold catalyst. Once the hydrogen molecule is dissociated on Pd–Ag alloy surfaces, hydrogenation of cyclohexene can occur over gold surfaces. Although the nobleness of bulk gold for hydrogen dissociation has been supported by quantum chemistry calculations,[10] hydrogen can be dissociated by the low-coordinated edge or corner atoms in gold nanoparticles at 298–373 K.[11] It has also been suggested that both the shape and size of gold particles are important for hydrogen dissociation.[12]

The active sites in gold catalysts have already been discussed for CO oxidation.[2,13–17] The majority of active gold catalysts are composed of gold nanoparticles in epitaxial contact with the metal oxide supports.[2,18] Charge transfer from an oxide support to gold nanoparticles was reported to form negatively charged gold particles[19,20] and to form a reactive gold–oxide interface.[21,22] Furthermore, it has been clearly demonstrated that some types of catalytic reactions take place at the periphery around the metal particles attached to metal oxide support.[23,24] It is an unanswered question whether the genesis of catalytic activity can be correlated to the increased fraction of edge or corner atoms, to a change in the electronic properties of the gold nanoparticles themselves, or to the reactivity of the perimeter interface around the gold particles in contact with the oxide supports. Herein we report that gold is no longer noble and can dissociate H_2 at a temperature below 400 K when it is deposited as clusters smaller than 2 nm on TiO_2(110) single crystals. Interestingly, we found that the H_2 dissociation activity depended on the number of gold atoms located at the circumference of gold nanoparticles on TiO_2, thus supporting the perimeter interface hypothesis.

Gold nanoparticles were deposited on rutile TiO_2(110) single crystal surfaces by a cathodic ark plasma (CAP) deposition method. The size of the gold particles can be tuned by adjusting the condenser capacity of the CAP (Figure 1). The gold coverage of all samples was fixed to one monolayer equivalent (MLE). For all condenser capacities used, the gold particles deposited were almost hemispherical in shape, which was confirmed by atomic force microscopy measurements, whereas their mean diameters increased with an increase in condenser capacity. Small gold clusters with a mean particle diameter of 1.3 nm (composed of approximately 55 atoms) were observed on the TiO_2(110) surfaces when a condenser capacity of 360 μF was used. The mean diameters of the gold particles were 2.5 and 4.2 nm at condenser capacities of 720 and 1440 μF, respectively, thus indicating that the diameter of gold particles increased by about 1.5 nm when the condenser capacity was doubled. At a condenser capacity of 2200 μF, the size distribution of gold particles was bimodal (4.3 and 5.8 nm), from which the mean particle diameter was calculated to be 5.5 nm. Thus, the size of gold particles deposited on a single crystal of TiO_2 can be controlled in the range of 1–10 nm.

The activation of molecular hydrogen on gold surfaces has recently been investigated by density functional theory (DFT) calculations. Corma et al. reported that gold atoms that are active toward H_2 dissociation must be neutral or have a net charge close to zero, be located at a corner or an edge (less coordinated positions), and not be directly bonded to the support.[25] To clarify the nature of active sites for H_2 dissociation on supported gold nanoparticles, we studied the H_2–D_2 exchange reaction over a variety of model surfaces. The reaction was performed with a mixture of 6 Torr H_2 and 6 Torr D_2 in batch mode, and the reaction gases were analyzed by quadrupole mass spectroscopy. The H_2–D_2 exchange reaction was carried out at 300–500 K on gold single crystals of Au(111) and Au(311) as well as on TiO_2(110) single-crystal surfaces (Figure S1 in the Supporting Information). No HD formation was observed at any single-crystal surfaces, thus

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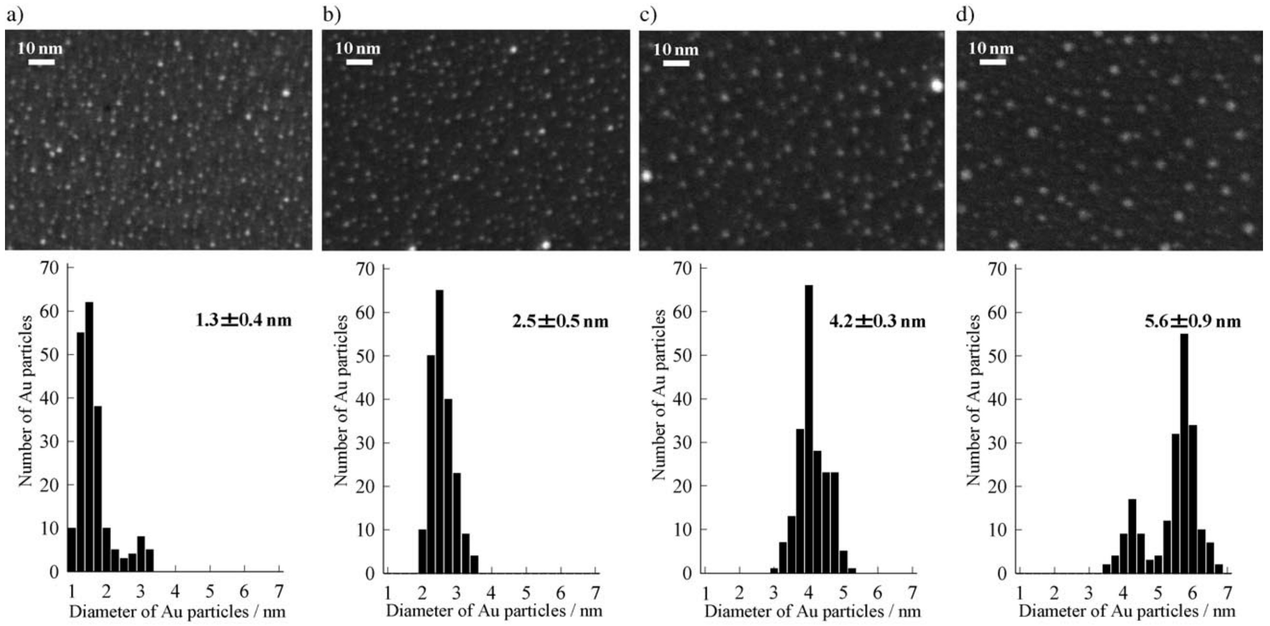

Figure 1. Field-emission SEM images (top) and the size distributions (bottom) of gold particles deposited on the $TiO_2(110)$ surfaces at various condenser capacities: a) 360, b) 720, c) 1440, and d) 2200 μF. One MLE of gold was deposited on each TiO_2 surface at an arc voltage of 70 V, at room temperature, and under 10^{-9} Torr. The numbers in the size distribution diagrams indicate mean diameters and standard deviations of gold particles.

indicating that gold metal and TiO_2 surfaces did not dissociate the hydrogen bond. Then, the rates of HD formation were measured at 425 K over $Au/TiO_2(110)$ surfaces with different sizes of gold particles; for such materials HD was produced, implying that hydrogen dissociation occurred. The initial rates of HD formation were obtained from the slopes of plots of HD molecules formed versus reaction time. The rate of HD formation increased with a decrease in gold particle size and markedly increased below 2 nm (Figure S2 in the Supporting Information).

We examined the rate of HD formation and the turnover frequencies (TOFs) for each catalyst sample with the same loading of gold (1 MLE) as a function of mean gold particle diameter. The TOFs were calculated by normalizing the number of HD molecules formed per second to the total number of gold atoms at the perimeter interfaces, which was estimated from the perimeter length of the gold particles and the interatomic distance of gold (0.288 nm). The rates of HD formation sharply increased below 2 nm, whereas the TOFs are almost constant regardless of the mean gold particle diameter, suggesting that the active sites for H_2 dissociation are the gold atoms located at the periphery around gold particles attached to TiO_2 and that the catalytic activity for H_2 dissociation is correlated neither to a change in the fraction of edge or corner sites nor to a change in the electronic nature induced by the quantum size effect (Figure 2).

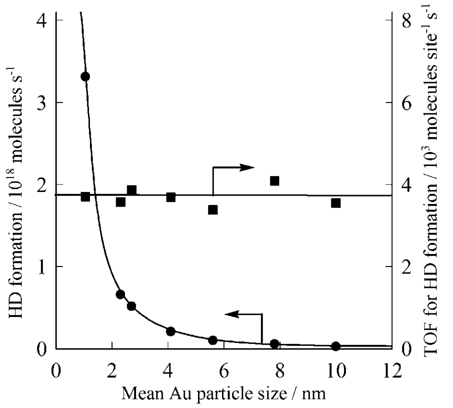

Figure 2. The rate of HD formation for each catalyst sample with the same gold loading (1 MLE) and the turnover frequencies based on the length of the perimeter interface as a function of the mean diameter of gold particles. H_2–D_2 exchange reaction was performed in batch mode using a mixture of 6 Torr H_2 and 6 Torr D_2 at 425 K.

To confirm whether the gold atoms located at the periphery of the particles are the active sites for H_2 dissociation, kinetic behavior was investigated for 1 MLE gold deposited on $TiO_2(110)$ for differing mean diameters of gold particles (Figure 3). The initial rates of HD formation were fist-order with respect to the total pressure of H_2 and D_2, irrespective of the size of gold particles. The rate constants of HD formation strongly depended on the mean diameter of gold particles. The H_2–D_2 exchange reaction rate over gold particles of 1.3 nm was about 30 times as high as that over gold particles above 5.5 nm. However, the slopes of the Arrhenius plots were nearly equal for all $Au/TiO_2(110)$ model surfaces. The apparent activation energy for the H_2–D_2 exchange reaction was calculated to be 36.2–36.6 kJ mol^{-1} and was identical, regardless of the differences in the diameters of the gold particles. This result supports the proposal that the nature of active sites for H_2 dissociation on $Au/TiO_2(110)$ did

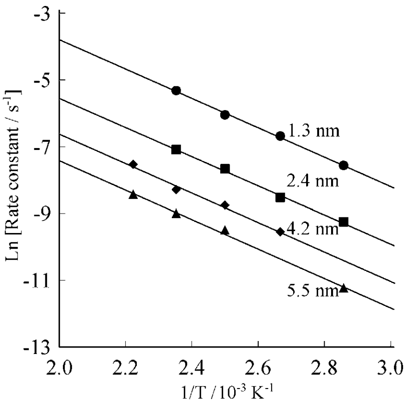

Figure 3. Arrhenius plots of the rate constants of HD formation over the 1 MLE Au/TiO_2(110) surfaces having different mean diameters of gold particles. The H_2–D_2 exchange reaction was performed in batch mode using a mixture of 6 Torr H_2 and 6 Torr D_2 at 350–450 K. The rates were obtained from the slope of the tangent of the conversion–time curves in HD formation at time $t = 0$. The rate constants were calculated based on the first-order reaction, which was experimentally confirmed.

not vary with the size of gold particles. It is likely that the H_2–D_2 exchange reaction takes place on the gold atoms located at the perimeter interfaces around gold particles and that the nature of the catalytically active sites is the same, irrespective of the size of gold particles.

The size of gold particles is known to markedly affect the catalytic activity, and, in particular, lead to high catalytic activity below 5 nm.[2,26,27] The metal oxide supports significantly change the selectivity as well as the catalytic activity of gold nanoparticles.[2] Herein, we found that the contact or junction between gold and the TiO_2 support is crucial to the formation of active sites. To confirm the H_2 dissociation reactivity at the Au–Ti interface, the H_2–D_2 exchange reaction rate was measured over Ti deposited on a Au(111) single crystal. An inversely supported model gold catalyst, Ti/Au(111), was prepared by depositing Ti on Au(111) by using an electron beam evaporator. No HD formation was observed on the Ti/Au(111) surfaces, indicating that the Au–Ti metallic interface had no H_2 dissociation ability (Figure S3 in the Supporting Information). Then, the Ti/Au(111) surfaces were oxidized at 623 K for 10 min in 3×10^{-7} Torr O_2. After the oxidation, the Ti $2p_{3/2}$ binding energy shifted by 4.8 eV to 459.1 eV and an O/Ti atomic ratio of about 2.0 was determined by X-ray photoelectron spectroscopy (XPS). This peak position was in good agreement with the Ti $2p_{3/2}$ binding energy of TiO_2(110), thus indicating that the deposited Ti species on Au(111) were completely oxidized to stoichiometric TiO_2.[28] When the Ti metal on Au(111) was oxidized to TiO_2, the H_2–D_2 exchange reaction proceeded on the TiO_2/Au(111) surfaces (Figure S3 in the Supporting Information).

The rate of reaction was first-order at 350–500 K, identical to that over Au/TiO_2(110). Temperature dependence of the H_2–D_2 exchange reaction was also measured over the TiO_2/Au(111) ($\Theta_{Ti} = 0.6$) model surfaces at 350–500 K. A coverage Θ of 1 corresponded to the number of surface Au atoms (1.39×10^{15} atoms cm^{-2}). The apparent activation energy for the H_2–D_2 exchange reaction was calculated to be 36.2 kJ mol^{-1}. These values are identical to the experimental values obtained over the Au/TiO_2(110) surfaces, thus allowing the conclusion that the active sites for H_2 dissociation in gold catalysts are located at the perimeter interfaces between gold and TiO_2 (Table S1 in the Supporting Information).

Another possibility to explain the markedly high catalytic activity of small gold clusters with a mean diameter of 1.3 nm (about 30 times that of 5.6 nm particles) would be a significant change in the electronic state of the gold clusters. The first-principle calculations of the bonding energies of gold and TiO_2 showed that the bonding strength of gold was much weaker on the stoichiometric surface of TiO_2 (present work) than on oxygen-rich and metal-rich surfaces,[29] whereas a very strong interaction leading to positively charged gold nanoparticles was reported for stoichiometric TiO_2 surfaces by the groups of Corma[25] and of Besenbacher.[30] On the other hand, positively charged Au atoms have been reported to be unable to activate H_2.[25] The Au $4f_{5/2}$ and $4f_{7/2}$ binding energy obtained by XPS of Au/TiO_2(110) model catalysts increased gradually, but only slightly (0.4 eV), with a decrease in the mean diameters of gold particles down to 1.3 nm (Figure S4 in the Supporting Information). Therefore, the change in the electronic structure of gold clusters by quantum size effect is marginal and may not explain the markedly large size effect in hydrogen dissociation in the present catalytic system.

The results reported herein are surprising in that the perimeter interfaces are the active sites for hydrogen dissociation, as is the case for molecular oxygen activation in low-temperature oxidation of CO.[2] The results also imply that by tuning the size of gold particles and by choosing proper metal oxide supports, a novel type of heterogeneous catalyst will emerge showing unique product selectivity completely different from that obtained by palladium and platinum catalysts. If the gold nanoparticles supported on stoichiometric TiO_2 become positively charged, owing to a much stronger adhesion at the Au–TiO_2 interface,[29–31] positively charged gold atoms may exist at the interfaces between the gold particles and TiO_2. Taking into account the possibility that positively charged gold atoms are not able to activate H_2,[25] the active sites for H_2 dissociation may not consist of gold atoms alone but instead may be formed by a combination of gold atoms and oxygen atoms from TiO_2 at the interfaces between these two components.

Experimental Section

The experiments were carried out in an ultrahigh-vacuum apparatus equipped with an X-ray photoelectron spectrometer, a quadrupole mass spectrometer (QMS), and a batch reactor. Field emission scanning electron microscopy measurements were performed in the secondary electron imaging mode, 30 kV accelerating voltage, and 10 μA emission current.

Single crystals of TiO_2(110) ($8 \times 8 \times 0.5$ mm, 99.999 % purity) were used as supports for the Au/TiO_2 model catalysts, which were cleaned by three cycles of Ar^+ sputtering and annealing at 900 K under vacuum after oxidation at 900 K for 90 min in 200 Torr oxygen. Single-crystal discs of Au(111) and Au(311) (8 mm diameter, 1 mm thickness, 99.999 % purity) were polished on only one side. The surfaces were cleaned by cycles of Ar^+ sputtering and annealing at 900 K under vacuum.

Gold was deposited onto the TiO_2(110) surfaces by cathodic arc plasma deposition (ULVAC, ARL-300) at 300 K, at 70 V arc voltage and 360–2200 μF condenser capacity under 10^{-9} Torr. The gold coverage was fixed to 1 MLE by controlling the generation frequency of the arc. The deposition of Ti on the Au(111) surfaces was performed by evaporation from a Ti rod (1.5 mm diameter) with an electron beam evaporator (AVC AEV-1). The Ti deposition rate was 0.05 MLE min^{-1} at a constant flux of 10 nA. The TiO_2/Au(111) model surfaces were produced by oxidizing the Ti deposited on a Au(111) surface at 623 K for 10 min in 3×10^{-7} Torr O_2.

The H_2–D_2 exchange reaction was carried out using a mixture of 6 Torr H_2 and 6 Torr D_2 at a sample temperature of 350–450 K in a batch reactor. The concentrations of H_2, D_2, and HD gases were obtained by monitoring the pressures of mass numbers 2, 4, and 3, respectively, with QMS.

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